

Relative proton transfer abilities of acids and alcohols in gas phase and solutions

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Abstract. The present paper applies a method, based on SCF CNDO MO charge densities and assumption of the validity of the virial theorem, for calculation of relative proton affinities of alcohols, and substituted and unsubstituted carboxylic acids in the gas phase. The paper also chalks out a path for calculation of their relative acidities in solution phase by utilising a solvation energy equation and binding energy data in the gas phase. The results obtained by the present method are mostly in agreement with ion cyclotron resonance mass spectrometric experimental studies. The method has also been applied to cover the cases of amines in the gas phase.

Keywords. Gas phase proton transfer; acidity order; binding energy; solvation energy.

1. Introduction

During the past two decades, ion cyclotron resonance (ICR) mass spectrometric experiments (Brauman and Blair 1968, 1970; Baird and Dewar 1969; McIver and Miller 1974; Yamdagni and Kebarle 1976; Wolf *et al* 1979) on acids, alcohols, alkanes and many other compounds in the gas phase have led to results which have been utilised in determining the relative strengths of acids and the relative acidities of alcohols and alkanes in the gas phase. The acidity order in the gas phase is found, in many cases, to be the reverse of what is observed in solution. Such experimental revelations have simultaneously encouraged attempts (Wiberg 1968; Lewis 1969; Hamadi *et al* 1979; Eades *et al* 1980), based on one or other form of the molecular orbital theory, to calculate the gas phase acidity order theoretically.

A perusal of ICR and similar experimental work (Brauman and Blair 1968, 1970; Yamdagni and Kebarle 1976) and their interpretations of the relative acidities in the gas phase are based on the assumption of the existence of equilibrium for these species present at very low concentrations. A search of literature for the theoretical calculations on proton transfer in the gas phase reveals that quite a few of these are mainly based on different forms of MO theories ranging from parametrised SCF methods to *ab initio* ones (Wiberg 1968; Lewis 1969; Hamadi *et al* 1979; Eades *et al* 1980, 1981). The *ab initio* MO treatment has been extended to

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many molecules, small and big (Richards and Horsley 1970; Hehrer *et al* 1986). The explicit *ab initio* calculations of acidities by Eades *et al* (1980) with zero point energy corrections pertain to H_2O , H_3O^+ , NH_3 , NH_4^+ , H_2S , H_3S^+ . These data are helpful in setting up the scale of intrinsic proton affinity in the gas phase. Of the common parametrised SCF MO methods, the MNDO/MINDO technique gives almost accurate values of heats of dissociation (Dewar *et al* 1972) and hence binding energies necessary for calculation of acidity. The CNDO/INDO methods with fewer parametric assumptions (Pople & Beveridge 1970) yield binding energies of molecules which, in most cases, differ very widely from the true values. In spite of this, the sequence of relative acidities of alkanes, alcohols, fatty acids and halo substituted fatty acids in the gas phase is correctly predicted (Wiberg 1968; Lewis 1969; Yamdagni and Kebarle 1976; Brauman and Blair 1968, 1970).

We thus have, apart from intermediate versions, two extremes—the difficult *ab initio* MO process with incorporation of zero point energy corrections and the easily accessible CNDO process for calculation of acidity in the gas phase. The present work deals with this acidity problem from the CNDO perspective without, however, the latter's inherent limitation of incorrect binding energy values. Additionally and more importantly it deals with relative acidities in the solution phase starting from the calculated data pertaining to gas phase acidities.

2. Method

Recently, a quasi-classical method (Rakshit and Mukherjee 1984; Rakshit and Hazra 1988) has been described by which the binding energies of ions and molecules in singlet ground states can be calculated fairly accurately. The cardinal features of this method are the employment of the virial theorem, and electrostatic concepts together with the charge densities and exchange energies of the CNDO molecular orbital theory. The latter two are eigenvector-dependent properties and are among the dependable CNDO-based molecular data. While the process of indirect calculation of binding energy by the CNDO method depends on, among others, the parametric values of core and resonance integrals, the modified method considers the diatomic exchange integrals in the direct computation of binding energies and shuns the parametric values.

The relevant expression of binding energy of molecules (1) and ions (2) are as:

$$E_{\text{bin}} = \frac{1}{2} \left[\sum_i \frac{q_i^2}{2r_i} + \sum_{i<j} \frac{q_i q_j}{r_{ij}} - \sum_{A<B} \frac{1}{2} (1+k_n \cdot n) \times \right. \\ \left. \times \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu}^2 \gamma_{AB} \right] \times 27.2 \text{ eV}, \quad (1)$$

$$E_{\text{bin}} = \frac{1}{2} \left[\left\{ \sum_i \frac{q_i^2}{2r_i} + \sum_{i<j} \frac{q_i q_j}{r_{ij}} \right\} - \sum_{A<B} \frac{1}{2} (1+k_n \cdot n) \times \right. \\ \left. \times \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu}^2 \gamma_{AB} + \Delta E'_{\text{ex}} \right] \times 27.2 \text{ eV}, \quad (2)$$

where $P_{\mu\nu}$ is the element of the charge density matrix; q_i 's are the atomic charge densities; k_n , an analytical parameter; n , the number of valence orbitals used in LCAO and γ_{AB} is the diatomic repulsion integral between a pair of electrons.

Our approach rests on finding the enthalpy change, ΔH , of the reaction;



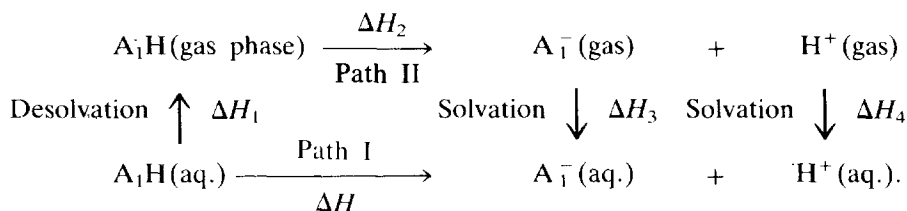
where, for acids, A_1^- and A_2H are the anion of an acid and a second acid respectively in the gas phase. For alcohols, A_1^- is an alkoxide ion and A_2H a second alcohol. It is assumed that $\Delta G \approx \Delta H$, ΔS of the reaction being very small. A negative ΔG would indicate that the preferred direction of proton transfer in (3) is from left to right and thus A_2H is a stronger acid than A_1H . The evaluation of ΔH per molecule or ion is calculated by using (1), (2) and (4)

$$\Delta H = \{E_{\text{bin}(A_1H)} + E_{\text{bin}(A_2^-)}\} - \{E_{\text{bin}(A_1^-)} + E_{\text{bin}(A_2H)}\}. \quad (4)$$

The acidity order in the aqueous solution phase can be obtained by calculating $\Delta G (\approx \Delta H)$ of the dissociation:



via path II of the scheme (shown below):



ΔG via path I is the same as that via path II.

$$\Delta G \approx \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4, \quad (5)$$

where ΔH_1 is the desolvation energy and ΔH_2 the enthalpy change of gas phase ionisation of A_1H . ΔH_3 and ΔH_4 are the solvation energies of the ions A_1^- and H^+ respectively.

Calculations of desolvation and solvation energies can be done satisfactorily by using a method (Rakshit and Mukherjee 1984) based on the charge density matrix or more specifically on atomic charge densities q_i , q_j 's, using the CNDO process. The relevant expression in kcal/mol, is:

$$E_{\text{hydr}} = -627 \cdot 1 \left[\left(\sum \frac{q_i^2}{(r_i + pr_w)} + \sum_{i < j} \sum \frac{q_i q_j}{r_{ij} + qr_w} \right) \left(1 - \frac{1}{D} \right) \right], \quad (6)$$

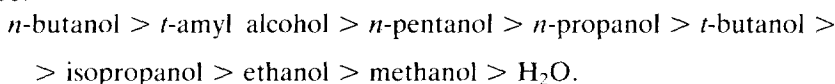
where $(r_i + pr_w)$ is the radius of the ion in the aquated state and D the dielectric constant.

This yields ΔH_1 , ΔH_3 and ΔH_4 of (5). The value of ΔH_2 is given by the binding energy difference of $\{A_1^- + H^+\}$ and A_1H .

3. Results and discussion

Having thus referred to the methods of calculation, (1), (2), (4) and (5), we now tabulate the data for alcohols and different carboxylic acids both for gas phase and solution phase proton transfers.

A scrutiny of table 1 suggests the following decreasing order of acidity in the gas phase:



Experimentally (Brauman and Blair 1968, 1970; McIver *et al* 1974) the order found is practically the same except that Brauman and Blair group *t*-butanol and *n*-pentanol together as having practically the same gas phase acidity. From the table 1, one can also divine that a primary alcohol is more acidic in the gas phase than the corresponding isomeric secondary or tertiary alcohol. This, however, does not hold for *n*-pentanol and the amyl alcohol.

Employing the method mentioned earlier and using (5), the relative order of acidity of the alcohols in aqueous phase (dielectric constant 78.5 at 25°C) has been calculated and these are incorporated in table 2.

Table 1. Gas phase acidity of alcohols.

A ₁ H	A ₂ H	Binding energy (eV)				ΔH (k cal/mol)
		A ₁ H	A ₁ ⁻	A ₂ H	A ₂ ⁻	
Water	Methanol	-9.52	-7.28	-21.32	-19.17	-2.07
Methanol	Ethanol	-21.32	-19.17	-33.51	-32.26	-20.75
Ethanol	Isopropanol	-33.51	-32.26	-46.01	-45.03	-6.22
Isopropanol	<i>t</i> -Butanol	-46.01	-45.03	-58.65	-57.95	-6.45
<i>t</i> -Butanol	<i>n</i> -Propanol	-58.65	-57.95	-45.36	-44.86	-4.61
<i>n</i> -Propanol	<i>n</i> -Pentanol	-45.36	-44.86	-70.08	-69.77	-4.38
<i>n</i> -Pentanol	<i>t</i> -Amyl alcohol	-70.08	-69.77	-70.40	-72.70	-60.16
<i>t</i> -Amyl alcohol	<i>n</i> -Butanol	-70.40	-72.70	-57.93	-57.78	-56.47

Table 2. Enthalpy changes for proton transfer reactions in solution phase.

A ₁ H	A ₂ H	Solvation energy (k cal/mol) (calculated)				ΔH (k cal/mol)
		A ₁ H	A ₁ ⁻	A ₂ H	A ₂ ⁻	
Ethanol	Methanol	-4.45	-78.34	-4.07	-84.29	-6.33
Isopropanol	Ethanol	-4.91	-73.93	-4.45	-78.34	-4.87
<i>t</i> -Butanol	Isopropanol	-5.12	-70.49	-4.91	-73.93	-3.65
<i>t</i> -Amyl alcohol	<i>t</i> -Butanol	-20.54	-81.47	-5.12	-70.49	-4.44
<i>n</i> -Propanol	Ethanol	-4.34	-75.97	-4.45	-78.34	-2.26
<i>n</i> -Butanol	<i>n</i> -Propanol	-4.45	-70.98	-4.34	-75.97	-5.10

The acidity order in solution (aqueous phase) is:

Methanol > ethanol > isopropanol > *t*-butanol > *t*-amyl alcohol.

This order is consistent with the general interpretation of the reversed effect of increasing size of the alkyl groups on the gas and solution phase acidities of the alcohols (Brauman and Blair 1968). While reliable experimental data on the relative acidities of the aqueous solutions of alcohols are rather scarce, a few such dependable data on CH₃OH, C₂H₅OH and some other alcohols have been reported (Pesce 1962) and these support our conclusions.

The decreasing enthalpies of solvation of alcohols in DMSO calculated from gas phase experimental enthalpy changes and other thermochemical data (Arnett *et al* 1974) is also indirect support for our conclusions.

The acidity order of certain carboxylic acids has been studied both for gas phase and solution phase proton transfers. The calculated data are given in table 3 for the unsubstituted and the substituted acids.

The order of acidity in the gas phase, based on $\Delta G (\approx \Delta H)$ of the full conversion, is:

- i) *n*-valeric acid > *n*-butyric acid > propanoic acid > acetic acid > formic acid.
- ii) Trifluoroacetic acid > difluoroacetic acid > fluoroacetic acid > acetic acid.
- iii) Trichloroacetic acid > dichloroacetic acid > chloroacetic acid > acetic acid.

The experimentally observed order (ICR) is based on the determination of $\Delta G^\circ = (-RT \ln K)$.

The predictions from the calculated results are in good agreement with the experimental gas-phase order (Yamdagni and Kebarle 1973) except that the ICR experiment places formic acid higher than butyric acid. The reverse order of calculated acidity in aqueous solution is apparent for the *n*-carboxylic acids, where acidity decreases from acetic to butyric acid. This order in solution is confirmed by the experimental *pK* values of the acids (March 1977). However, valeric acid as calculation shows is less acidic than butyric acid. The calculated data are incorporated in table 4.

Table 3. Gas phase acidity of carboxylic acids

A ₁ H	A ₂ H	Binding energy(eV)				ΔH (k cal/mol)
		A ₁ H	A ₁ ⁻	A ₂ H	A ₂ ⁻	
Formic acid	Acetic acid	-20.90	-18.86	-33.36	-31.60	-6.45
Acetic acid	Propionic acid	-33.36	-31.60	-45.48	-44.42	-16.14
Propionic acid	Butyric acid	-45.48	-44.42	-58.15	-57.22	-3.00
Butyric acid	Valeric acid	-58.15	-57.22	-70.91	-70.14	-3.69
Acetic acid	Fluoroacetic acid	-33.36	-31.60	-32.22	-31.40	-21.67
Fluoroacetic acid	Difluoroacetic acid	-32.22	-31.40	-31.62	-31.07	-6.22
Difluoroacetic acid	Trifluoroacetic acid	-31.62	-31.07	-30.85	-30.60	-6.92
Acetic acid	Chloroacetic acid	-33.36	-31.60	-32.50	-30.85	-2.54
Chloroacetic acid	Dichloroacetic acid	-32.50	-30.85	-31.30	-29.68	-6.92
Dichloroacetic acid	Trichloroacetic acid	-31.30	-29.68	-29.33	-28.21	-11.53

Table 4. Order of acidity of carboxylic acids in solution phase.

A ₁ H	A ₂ H	Solvation energy(k cal/mol) (calc.)				ΔH (k cal/mol)
		A ₁ H	A ₁	A ₂ H	A ₂ ⁻	
Propionic acid	Acetic acid	-14.31	-88.40	-14.74	-90.56	-1.73
Butyric acid	Propionic acid	-13.56	-86.99	-14.31	-88.40	-0.66
Butyric acid	Valeric acid	-13.56	-86.99	-13.59	-110.50	-23.48

While the order of acidity of unsubstituted carboxylic acids in aqueous phase is well explained (table 4), the relative order of calculated acidities of the haloacetic acids in aqueous phase is not explained properly by the present method. The calculations of solvation energies (Rakshit and Mukherjee 1984) using CNDO/2 data may not be enough to explain the resonance stabilisation of haloacetate ions and their subsequent behaviour on aqutation. The entropy effects may also play a major role due to a possible geometry variation in solution. These additional factors should, perhaps, claim consideration in a theoretical treatment before comparison with experimental results is attempted.

It may incidentally be indicated that a difference appears in binding and solvation energies of chloroacetic acids when calculations are made with the inclusion or exclusion respectively of the *d*-orbitals in the basis set. The data, tabulated in the present paper, are those obtained by including the *d*-orbitals.

While discussing the acidity order in gas and aqueous phases, one is to note the average error in binding energies of the different species involved in such calculations. Since in general, the error is around 0.2 eV, a prediction of acidity order based on ΔH values around 4 kcal/mol may be somewhat tentative rather than being a certainty. Experimental results, however, do support the tentative conclusion. The tentativeness of conclusion does not arise in cases where prediction is made on the basis of ΔH values being 5 kcal/mol or more.

In conclusion it may be mentioned that the relative order of proton affinities of the amines in gas phase has also been calculated by the present technique. The decreasing order of gas phase proton affinities is



This finding is in agreement with experimental observation (Eades *et al* 1981b).

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